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Magnetic carbon – based nanocomposites for environmental applications: the case of arsenic and mercury removal from water†

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Abstract: Arsenic and mercury are two elements that cause great concern in aquatic systems due to their toxic effects to the living organisms, bioaccumulation with time and biomagnification along the food chain. For these reasons continuous attempts to develop efficient water treatment methodologies have been made. Here, we report the synthesis and characterization of magnetic carbon-based nanostructures to remove As and Hg from aqueous solutions, and their concentration in a solid phase, promoting their recycling. The nanocomposites combine the magnetic properties of cobalt and manganese spinel ferrites properties with the ones of graphite nanoplatelets, exhibiting good sorption properties. In model solutions the removal efficiencies reach values of 80% using only a few milligrams per liter of nanocomposite.

Keywords: water remediation; toxic elements; graphite nanoplatelets; spinel ferrites

1. Introduction

Water is an essential resource to all human activities and to life in general, which is distributed inequitably around the world, with some populations living under water scarcity – a situation that is becoming more usually due to the impact of climate change [1]. Additionally, industrialization, population grow, and their needs have also contributed to the degradation and scarcity of safe water. Consequently, water issue it was made central to all components of the EU Green Deal and to several United Nation Sustainable Development Goals, starting with SDG6 on «clean water and sanitation». The mitigation of disastrous consequences of safe water scarcity is a worldwide challenge, and the scientific community should assume the responsibility for providing solutions based on scientific knowledge [1].

Arsenic and mercury are two elements that cause great concern in the aquatic systems. The chronic exposure of individuals to As could cause several injuries like cancer, and cardiovascular diseases, and even chromosome aberrations. According to the World Health Organization, the guideline value for As in drinking water is 10 μg/l, but in different regions of the globe, As concentrations can reach values significantly higher than 50 μg/l [2]. Mercury is neurotoxic, volatile, persistent, and bioaccumulates in the organisms. Due to their toxicity it is important to continue the research to improve the existent pollution control technologies [3]–[7].

From the available water cleaning technologies, adsorption is one of the most attractive due to its efficiency, reasonable cost, and simple operation mode. This is important for developing countries and for this reason, the adsorption process is generally preferred

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since it meets this need due to its easy handling and the wide variation in available natural and synthetic sorbents. Additionally, because metal ions cannot be degraded by bioprocess and chemical reactions, currently adsorption is considered as the most effective way to remove metals and other inorganic elements from water [8].

Activated carbon was considered as one of the most successful adsorbents for many years due to its high adsorption capacity and thermal stability. Recently, graphene has been emerging as a promising sorbent for water treatment. However, for water applications, the graphene sheets exhibit problems such as poor solubility and tendency for agglomeration [9]. To overcome these limitations, researchers developed a few techniques to synthesize compounds, like graphene oxide and graphite-like nanoplatelets (GNP), which are structurally similar and can be produced by top-down methods from several carbon sources [10].

To facilitate the recovery of the sorbent after the treatment process we explored the preparation of magnetic nanocomposites. Magnetic field separation is more economical, selective, and rapid than filtration and centrifugation processes. The goal of this study was to synthetize nanocomposites that combine the sorption properties of GNPs with the magnetic properties of spinel ferrites of cobalt and manganese ($CoFe_2O_4$; $MnFe_2O_4$), conferring them the possibility of recovery from water when exposed to an external magnetic field. In line with the SDG6, we investigated the efficiency of these nanocomposites for adsorption of As and Hg from model solutions.

2. Materials and Methods

2.1. Chemicals

For the synthesis of the carbon-based composites the following chemicals were used without further purification: graphite flakes (EDM 99.95%, Graphit Kropfmühl), dimethylformamide (DMF, Carlo Erba), potassium hydroxide (KOH, Aldrich), potassium nitrate (KNO_3, Aldrich), iron sulfate ($FeSO_4 \cdot 7H_2O$, AnalaR NORMAPUR VWR chemicals), manganese sulfate ($MnSO_4 \cdot H_2O$, Merck), cobalt chloride ($CoCl_2 \cdot 6H_2O$, Merck), nitric acid (HNO_3, 63%, Merck), and ethanol (C_2H_5OH, PA, Carlo Erba).

For the batch experiments, certified commercial standards solutions of Hg ($Hg(NO_3)_2$, Merck) and As (H_3AsO_4, Merck) with a concentration of 1000±1 mg/l, and ultra-pure water (UPW) produced by a Millipore Integral 10 system, were used for the solutions preparation. Solutions of sodium hydroxide (NaOH) and nitric acid (HNO_3) were used for pH adjustments.

A Hg standard solution of 10 mg/l was prepared weekly in UPW by dilution from the certified standard solution of 1000 mg/l $Hg(NO_3)_2$. A second Hg standard solution of 100 μg/l in UPW was prepared daily from the first one, and it was used for preparing the calibration standards for the Hg quantification. A As standard solution of 10 mg/l was prepared weekly in UPW by dilution from a certified standard solution of 1000 mg/l H_3AsO_4, and it was used for the preparation of the calibration standards for As quantification.

2.2. Magnetic carbon-based nanocomposites synthesis

To obtain GNPs, graphite powder (5 g) was sonicated graphite (Sonics Vibra Cell Sonicator, VC70, 130 W, 20 kHz) in DMF (100 ml) for 5 h, in an ice bath replaced every 30 min. The presence of DMF facilitates the exfoliation of graphite by reducing the strength of the Van der Waals interactions between the adjacent layers of graphite. The GNPs were separated by centrifugation (1200 rpm, 20 min, Hettich, model rotofix), and the supernatant was transferred to a beaker, filtered, and washed repeatedly with water, and then ethanol. After, the solid was kept in a drying oven (Binder, model FD 23) at 40 °C until complete drying.

The MFe_2O_4/GNPs (M=Co or Mn) were prepared by in situ methodology preparing the spinel ferrites by oxidative hydrolysis in the presence of the GNPs. Briefly, deoxygenated water was added to 1.90 g of KOH and 1.52 g of KNO_3. This mixture was then heated at 60 °C (oil bath) under N_2 atmosphere and mechanically stirred (500 rpm, overhead stirrer, IKA). After the dissolution of the salts, GNPs (200 mg) were added to 25 ml of an aqueous solution containing 3.06 g of $FeSO_4 \cdot 7H_2O$ and 1.02 g of $MnSO_4 \cdot H_2O$. The resulting mixture was added dropwise to the alkaline solution and the stirring was increased to 700 rpm. This solution was left to react for 30 min. After, the mixture was left under N_2 at 90 °C for 4 h, without stirring. The resulting nanocomposite ($MnFe_2O_4$/GNPs) was collected by using a NdFeB magnet, and then repeatedly washed with water and ethanol, and dried in a drying oven (Binder, model FD 23) at 40 °C. For the synthesis of the $CoFe_2O_4$/GNPs, the 200 mg GNPs were added to 25 ml of UPW containing 3.06 g $FeSO_4 \cdot 7H_2O$ and 1.43 g of $CoCl_2 \cdot 6H_2O$.

2.3. Magnetic carbon-based nanocomposites characterization

All the synthesized composites were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), chemical analysis, Raman spectroscopy and magnetic characterization. To evaluate the morphological characteristics of the composites TEM analysis (Hitachi H-9000 TEM microscope) was performed. The structural characteristics of the composites were determined using X-ray diffraction. It was made sure the samples were completely dried, and subsequently the XRD spectra were obtained using a Philips X'Pert X-ray diffractometer equipped with a Cu Ka monochromatic radiation source, in the range $2\theta = 3.5–70$ °C. Raman spectra were obtained using a combined Raman confocal microscope (alpha 300 RAS+, WITec, Germany), equipped with Nd:YAG laser operating at 532 nm. The laser power used was 1mW. Magnetic measurements were performed using a Quantum Design MPMS3 SQUID-VSM. The Fe, Mn and Co composition was determined by microwave assisted acid digestion.

2.4. Removal of As and Hg from water

The capability of the MFe_2O_4/GNPs (M=Co or Mn) nanocomposites to remove Hg(II) and As(III) from model solutions was studied for mono element systems and different pH values. The removal capability of each material was assessed by exposing equal amounts of material (40 mg/l) to solutions of Hg(II) or As(IIII), containing initially 50 μg/l and 1000 μg/l, of the respective element. Batch experiments were carried out for 24 h in 100 ml-Schott© glass flasks at 22 °C, with stirring (250 rpm), after dispersion of the sorbent in an ultra-sound bath. At 0 and 24 h, 25 ml of water aliquots were collected, preserved with NO_3 (pH <2) and stored at 4 °C until quantification. The liquid-solid separation was done by using a NdFeB magnet.

The pH effect on the removal capability of the nanocomposites was also studied, covering the whole range of groundwater pH values (4 to 9), under the previous operational conditions. At 0 and 24 h, 25 ml of water aliquots were collected, preserved, and stored as previously described. The results, from materials comparison and pH effect were expressed in terms of removal efficiency (R_A):

$$R_A = (C_{A0} - C_A/C_{A0}) \times 100 \quad (1)$$

where C_{A0} and C_A (both μg/l) are, respectively, the initial and at time t concentration of each element (A) in solution.

The experiments were done in duplicate, and controls (UPW spiked with Hg(II) or As(III) in the absence of composite) were running in parallel with the experiments, under the same operational conditions. Solution pH was adjusted with 0.1 mol/l NaOH or 0.1 mol/l HNO_3 solutions. Mercury quantification was performed by cold vapor atomic fluorescence spectroscopy on a flow-injection cold vapor atomic fluorescence spectrometer (hydride/vapor generator PS Analytical Model 10.003, coupled to a PS Analytical Model 10.023 Merlin atomic fluorescence spectrometer), using $SnCl_2$ solution as reducing agent

(10% m/v). The limit of quantification was 0.1 μg/l Hg and the precision and accuracy <10%. Calibration curve (0.1 – 0.5 μg/l) was obtained using five standards prepared by diluting an appropriate volume of Hg standard solution (100 μg/l) in 2% HNO_3. Arsenic quantification was performed by hydride generation atomic fluorescence spectroscopy (PS Analytical Model 10.033 Excalibur atomic fluorescence spectrometer), using a $NaBH_4$ solution as reducing agent. The limit of quantification was 10 μg/l As and the precision and accuracy <10%. The samples were diluted 2 - 20 times, depending on the expected As concentrations, in 50 ml flasks with a 25% v/v HCl and 50% m/v KI with 10% m/v ascorbic acid solution (blank reagent). Calibration curve (10 – 80 μg/l) was obtained using five standards prepared by diluting the As standard solution (10 mg/l) in the blank reagent. All glassware used in the sorption essays was immerse in acid solution (HNO_3 25% v/v) for at least 12 h, then rinsed with UPW, before use.

3. Results and Discussion

3.1. Magnetic carbon-based nanocomposites characterization

3.1.1. TEM

The TEM images of the nanocomposites show the presence of $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles, with a spherical shape and an average size below 100 nm, attached to a lighter shaded substrate (GNPs) (Figure 1). The images also show different exfoliate degree of the graphite, with darker and lighter areas.

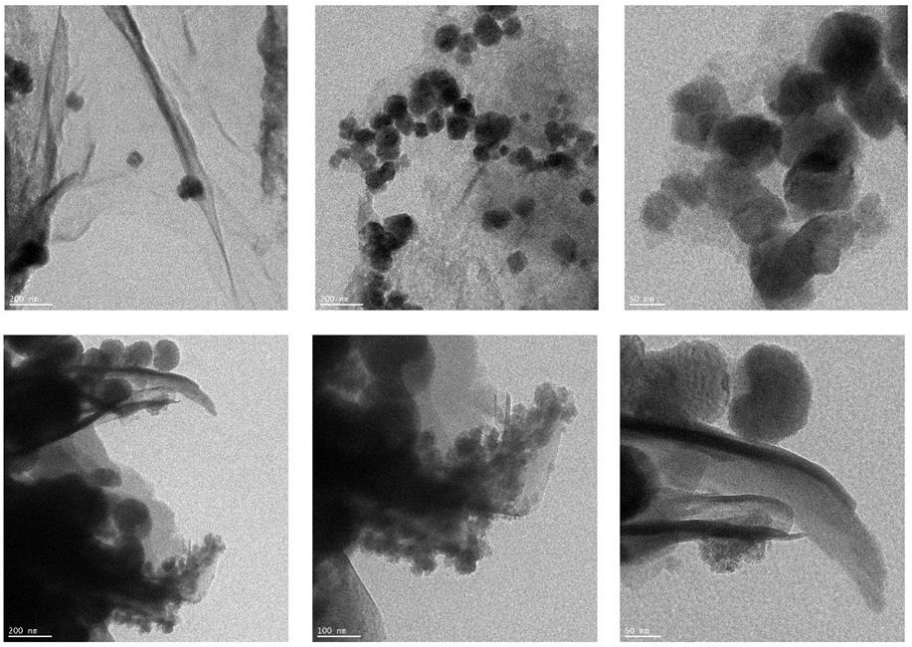

Figure 1. TEM images of $CoFe_2O_4$/GNPs (top) and $MnFe_2O_4$/GNPs (down).

The diffractograms of the nanocomposites (not shown) confirm the presence of cobalt- and manganese ferrites and GNPs. They display an intense peak at 2θ=26.56° that corresponds to the interlayer (002) planes distance d 0.34 nm in the graphitic structure. The remaining XRD peaks are indexed from the JCPDS cards for $CoFe_2O_4$ (No. 22-1086) and $MnFe_2O_4$ (No. 73-1964). The reflections at 2θ = 18.2º (111), 29.9º (220), 35.2º (311), 42.8º (400), 56.6º (511), 62.1º (440) (and the weak reflections at 2θ = 53.2º (422) and 89.0º (731)) confirmed the presence of $MnFe_2O_4$ in the $MnFe_2O_4$/GNPs. Thee $CoFe_2O_4$/GNPs XRD spectrum showed weaker reflections than the one of manganese ferrite. Although generally weak, the reflections at 2θ =18.3º (111), 35.5º (311), 43.2º (400), 57.1º (511), 62.1º (440) (and the very weak 30.6º (220) and 88.5º (731)) confirmed the presence of $CoFe_2O_4$.

The major bands in the Raman spectrum of the cobalt-ferrite nanocomposite reflected a typical spinel structure. The band at ~316 cm^{-1} was attributed to the E-site mode and bands at ~616 cm^{-1} and ~687 cm^{-1} were attributed to the A-site modes of $CoFe_2O_4$, in accordance with literature. Additional bands at ~474 cm^{-1}, ~190 cm^{-1} and ~290 cm^{-1} were attributed to the O-site mode, which reflects the local lattice effect in the octahedral sublattice. Also, for the manganese-ferrites, the spinel structure was reflected in the Raman spectrum. The band at ~333 cm^{-1} was attributed to the E-site mode and the band at ~627 cm^{-1} was attributed to A-site modes of $MnFe_2O_4$, in accordance with literature. Both nanocomposites show the D mode and the G and 2D peaks represented by the bands at ~1353 cm^{-1}, ~1580 cm^{-1} and ~2705 cm^{-1} characteristic of graphite.

The chemical composition of the nanocomposites is display in Table 1. The ratios of Fe/Co and Fe/Mn agree with the expected values.

Table 1. Co, Fe and Mn concentrations of the materials, determined via acid digestion.

Nanocomposite	[Fe] (mg/l)	[Co] (mg/l)	[Mn] (mg/l)	Fe/Co	Fe/Mn
$CoFe_2O_4$/GNPs	79.8	43.0	-	1.9	-
$MnFe_2O_4$/GNPs	80.9	-	40.2	-	2.0

From the magnetic measurements it was observed that both materials quickly approach towards saturation when exposure to an external magnetic field. The values obtained for the saturation magnetization at room temperature (30 emu/g), combined with the visual observations, evidence the necessary magnetic properties of both materials. More, the saturation magnetization values found are in the range of the reported values for similar sorbents and are appropriate for magnetically assisted removal.

3.2. Removal of As and Hg from water

In adsorption, the solution pH is one of the main parameters that may have a strong impact in the efficiency of the process. The removal efficiency obtained for each contaminant and nanomaterial, for different solution pH are shown in Figure 2.

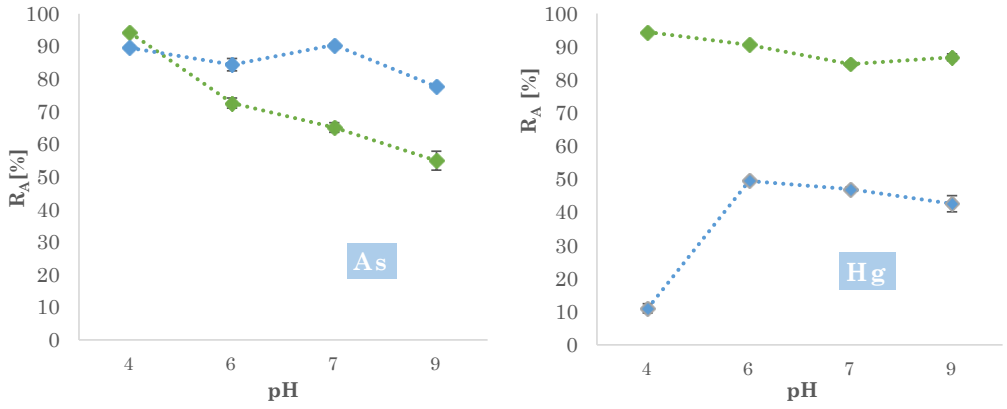

Figure 2. Removal efficiency of magnetic carbon-based nanocomposites toward arsenic (As) and mercury (Hg) ($MnFe_2O_4$/GNPs - green points; $CoFe_2O_4$/GNPs - blue points).

It was found that $MnFe_2O_4$/GNPs has a higher affinity for Hg than $CoFe_2O_4$/GNPs throughout the pH range studied, and similar efficiency to $CoFe_2O_4$/GNPs for As at pH 4.

For pH values between 6 and 9 the As removal efficiency is higher for $CoFe_2O_4$/GNPs than for $MnFe_2O_4$/GNPs. Differences in the removal efficiency between nanocomposites and toward contaminants may be related to the different speciation of As and Hg ions in solution according to pH and to the surface charge of the materials.

4. Conclusions

Magnetic carbon-based nanocomposites were successfully synthesized by attaching spinel ferrites ($MnFe_2O_4$ and $CoFe_2O_4$) to graphite nanoplatelets and evidence good sorption efficiency toward As and Hg water contaminants.

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